ABB

TOTALFLOW

Technical Bulletin 152

NGC Calibration Techniques (Technical Discussion)

Totalflow Technical Bulletin
Version 1.0, Revision AA (23 July 2007)

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Purpose

To utilize the NGC-82xx series gas chromatograph in a broader variety of application, ABB Totalflow has added the capability of using different types of calibration techniques. This paper will describe the differences between linear, exponential, and multiblend calibration.


Description

To better understand the differences between these calibration types, it is necessary to understand some basic concepts of the thermal conductivity detector which is used in the NGC. Thermal conductivity is basically the ability of a compound to conduct heat, and it is the differences in the amount of heat a compound can conduct that cause a response on the detector.

For example, the NGC uses a detector bead operating at a specific temperature. The detector circuitry is designed to hold the bead at a constant temperature. When the carrier gas (helium) is applied to the system, the bead tries to cool off because helium has a very high thermal conductivity and pulls a lot of heat away from the bead. The detector circuitry senses the change in temperature and pumps more power into the system to keep the bead at its preset temperature.

Now when the carrier gas pushes a peak of methane across the bead, the circuitry senses that not as much power is required to keep the bead at its preset temperature because methane does not pull as much heat off the bead as helium. This difference between the thermal conductivities of helium and methane is the mechanism which generates a peak.

TCD's have a limited linear dynamic range, there are a variety of factors which can influence this range. The first is the thermal conductivity of a binary mixture in itself is non-linear. There are also other factors that affect linearity, such as peak resolution, detector cell geometry and electronics.

Below is a response curve for methane. The concentration is plotted on the X axis, and raw peak area is plotted on the Y axis. Notice it is clearly not a straight line. So the problem is how to mathematically represent the response curve for a given component in order to insure the most accurate analysis.

Methane Response
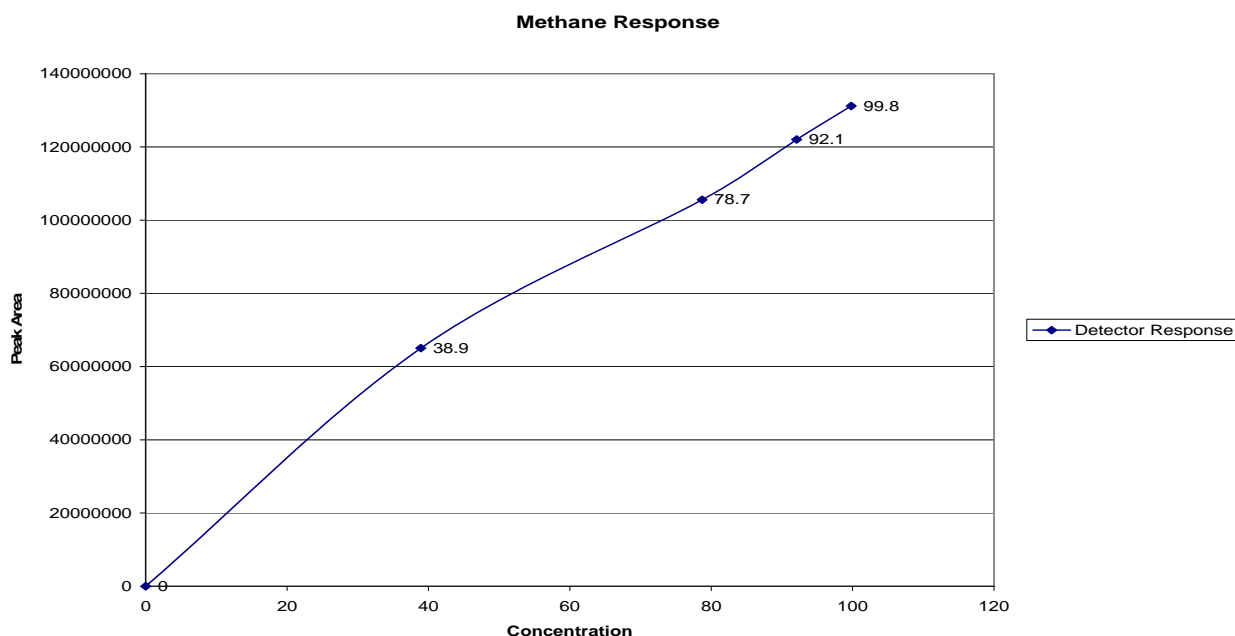
Linear Calibration

Linear calibration uses a linear curve which is defined by the equation,

$$y = Rf*x + b$$

where y = mol% of component
Rf = Response factor for given component
x = peak area
b = y intercept (offset)

A linear curve is often referred to as a single point calibration, but 2 points are actually required. This second point is the y-intercept, typically zero is used as the y-intercept, and this is known as force-thru zero.

Observe what happens when one does a linear calibration of methane at a concentration of 99.8 Mol%.

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Methane Response Curve and Linear Calibration Curve @99.8%
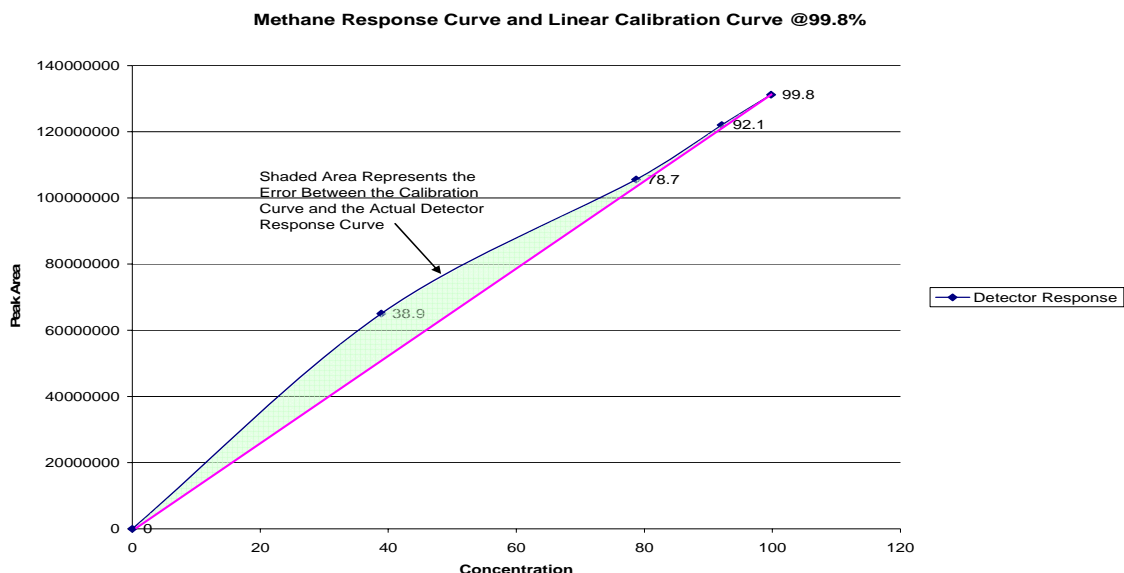
The large shaded area represents the amount of error between the linear calibration and the actual detector response. At 99.8Mol% the readings are identical as one would suspect, but the farther away from the 2 calibration points one gets, the larger the amount of error.

Next consider if one calibrates at 78.7 Mol%.

**Methane Response Curve and Linear Calibration Curve @ 78.7%**
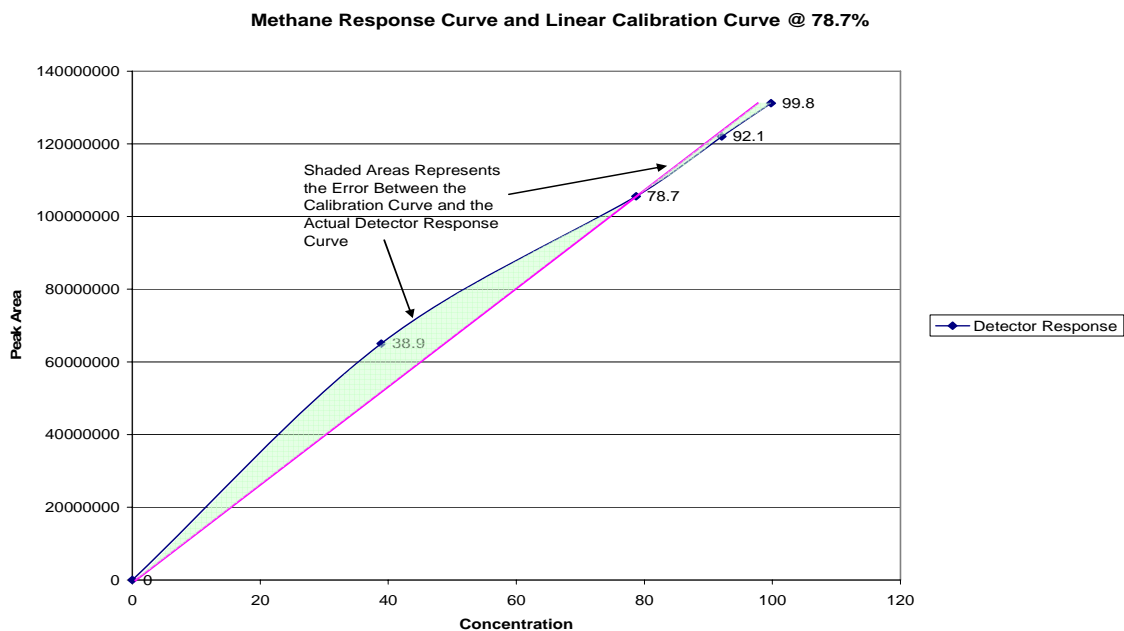
Notice this time, it has 2 shaded areas represented the amount of error between the calibration curve and the detector response curve. The analysis will still be the most accurate the closer one is to the actual calibration point.

The next graph was calibrated at 38.9 Mol%.

Methane Response Curve and Linear Calibration Curve @ 38.9%

Shaded Areas Represents the Error Between the Calibration Curve and the Actual Detector Response Curve
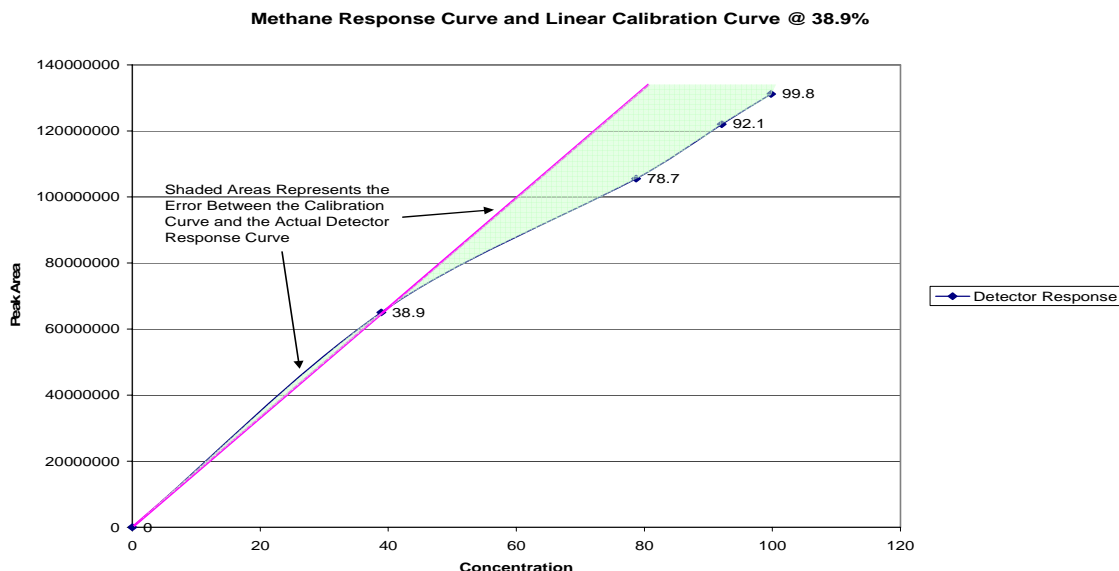
Detector Response

Notice how relatively close the 2 curves are between 0 and 40%, and then the large amount of error over 40% because the actual detector response changes but the linear curve does not.

Next consider using a y intercept other than zero, we still need 2 points to plot our straight line. Using the 38.9% and 99.8%, one can calculate a y intercept as shown in the next graph.

Methane Response Curve and Linear Calibration Curve Using Y Intercept

Shaded Areas Represents the Error Between the Calibration Curve and the Actual Detector Response Curve

Y- Intercept

Detector Response
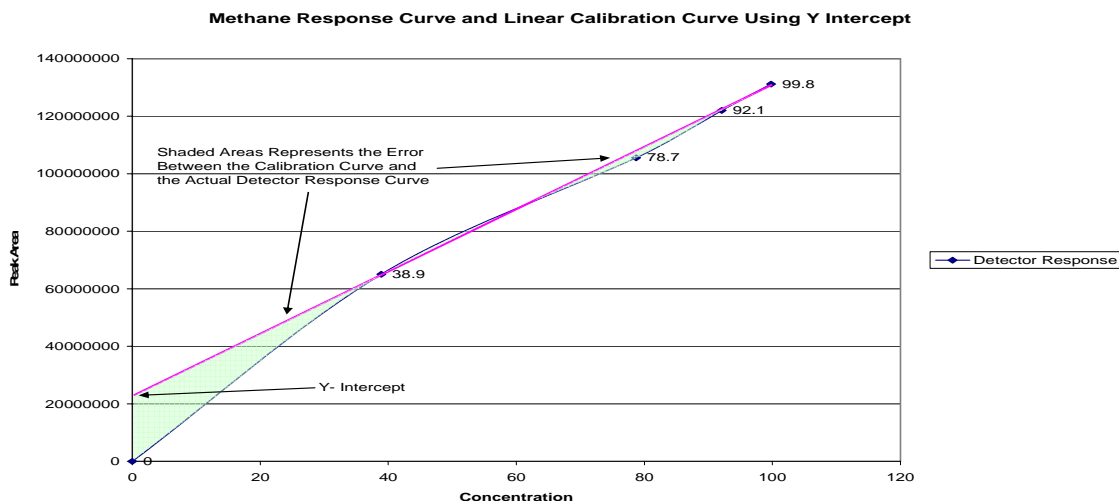
The error between the 2 calibration points has been greatly reduced using the y-intercept and the linear calculation. However, between 0 and 40% there is quite a bit of error.

It is clear that using a linear single point calibration reduces the linear dynamic range of the chromatograph. The operator must be very careful to make sure that he is calibrating within the range that he will be measuring to minimize the amount of error.

Exponential Calibration

In order to maximize the linear dynamic range, the calibration curve needs to fit the actual detector response curve as closely as possible. Totalflow has achieved this by replacing the single point linear curve with a multipoint exponential curve.

Each component has a curve which is predefined by the factory. Each curve is defined by 3 coefficients, the multiplier, the response factor, and the offset. The concentration of each component is calculated as follows.

$$Y = a * e(b*x) + c$$

Where
Y = Concentration (Mol%)
a = the multiplier
e = constant
b = response factor
x = peak area
c = offset

The following diagram is a plot of the exponential calibration curve vs the actual detector response curve.

Methane Response Curve vs Exponential Response Curve
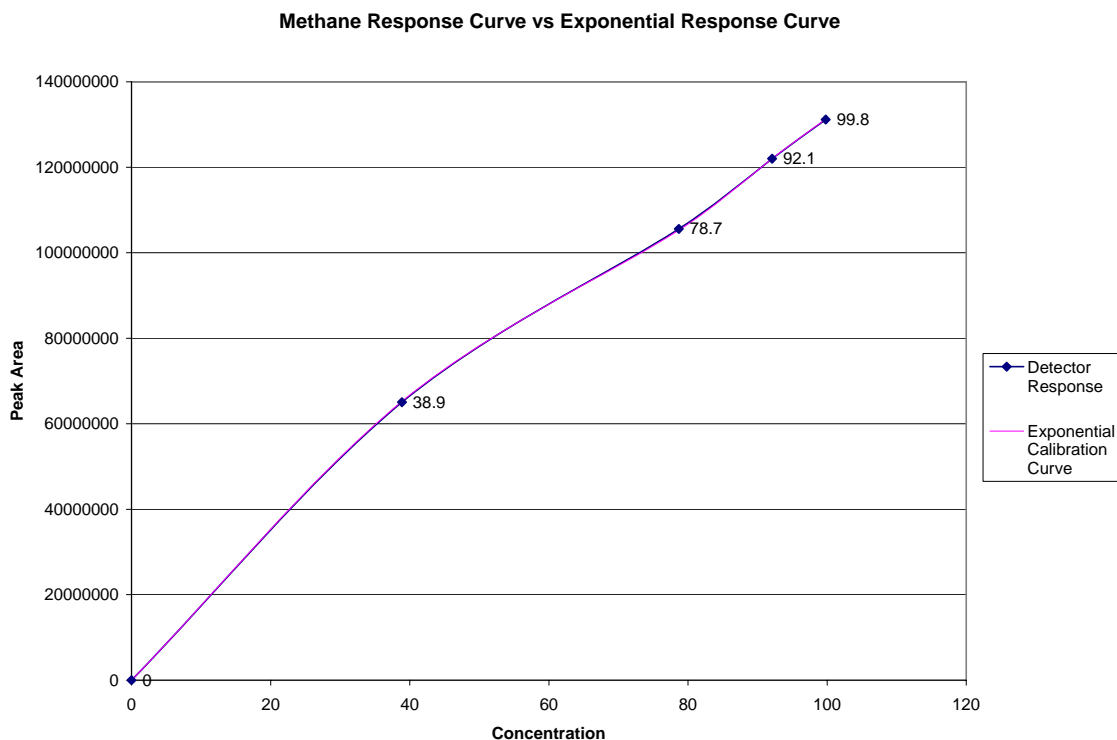
Notice how closely the calibration curve and the detector response mirror each other, greatly increasing the linear dynamic range of the analyzer.

It is worth noting that even though we are using a multipoint calibration curve, all the characterization is done at the factory. To perform day to day calibrations, a single calibration blend is all that is required.

It should also be noted that the exponential response factors are calculated differently than the single point linear response factors. If one plots the exponential factors versus molecular weight, it will not be a straight line.

If it is necessary to plot response factors versus molecular weight to validate a calibration gas, use the following formula.

RF = Certified Concentration/ Peak Area

This will yield a single point response factor for use in plotting, but the analyzer will still gain the benefits of the exponential calibration curve.

Multiblend Calibration

Multiblend calibration allows the user to generate multilevel calibration curves using their own calibration blends. On the Multiblend Cal Setup tab (shown below), the user defines which stream is used for each specific blend used in the calibration sequence.

The user also defines the number of purge cycles and actual calibration cycles used for each blend.

A maximum of 6 blends may be used. The NGC has only 4 stream inputs so whenever more than 4 blends are used, it is up to the operator to change cal blends on the appropriate stream at the appropriate time in the calibration sequence. If it is necessary to switch out bottles during the calibration procedure, it is vitally important that the sample lines are purged adequately, so as to not adversely affect the calibration curve.
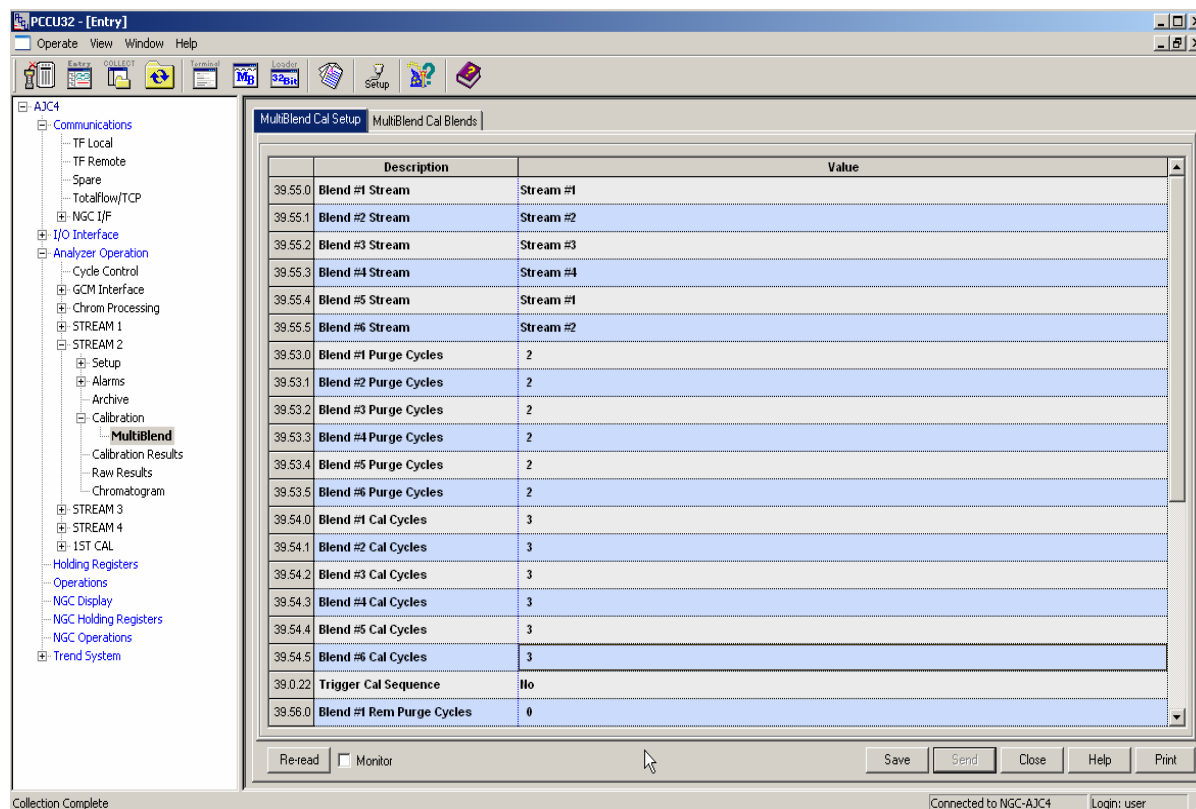
On the Multiblend Cal Blends tab (shown below), the user defines component concentrations for the different blends. If the "Use Zero" field is set to yes, the algorithm will use zero as an extra point and force the curve through zero.
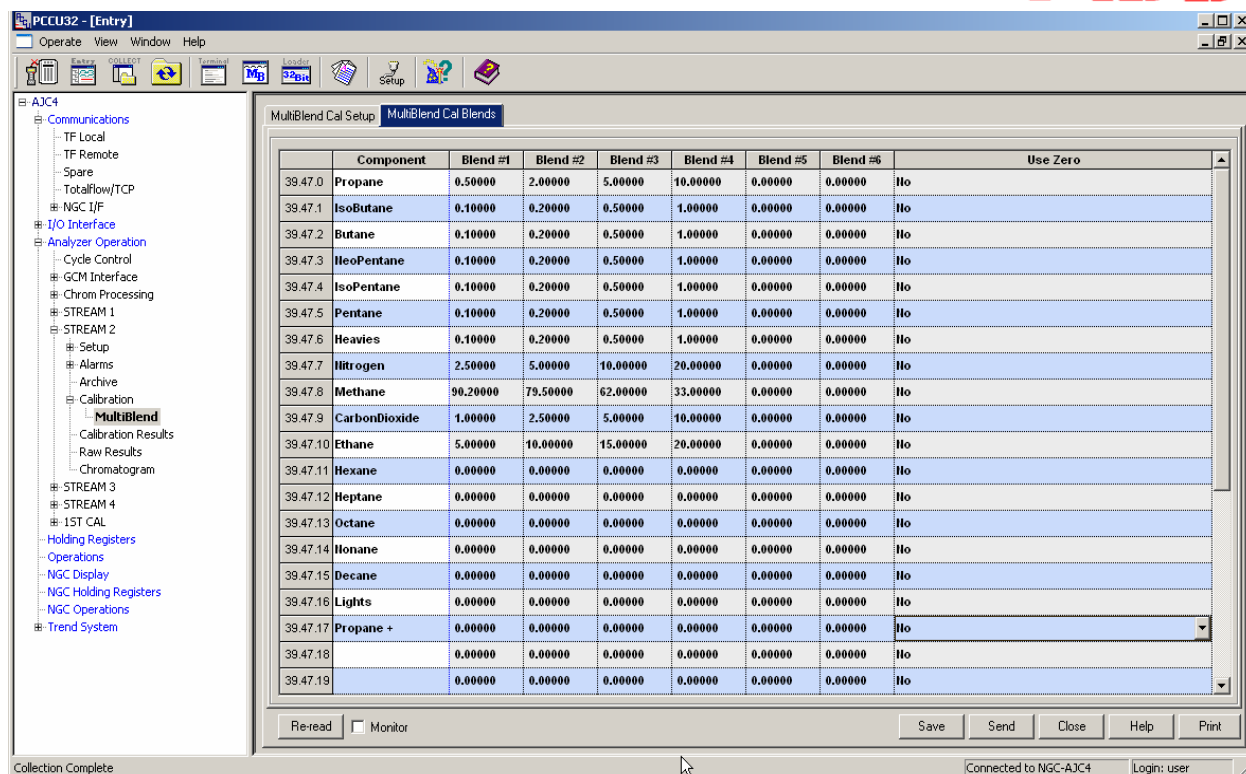
Multiblend calibration is not recommended for the majority of NGC applications. Multiblend calibration calculates an exponential curve just as exponential, but it requires all calibration blends being brought to the field. The customer may use up to 6 different blends with zero being the 7th level. The blends must be run in a specific sequence so the NGC will have all the data it needs to calculate the calibration curve. Detailed knowledge of the calibration sequence and sample handling techniques are required. Since these same calibration curves have been predefined at the factory, multiblend calibration is not recommended for the novice user.

Conclusion

As you can see from this discussion there are three different calibration techniques that can be utilized by the model NGC-82xx gas chromatograph. The exponential calibration technique is a combination of the easiest to implement along with providing accurate results. With this technique, the system is utilizing a multipoint calibration curve but all the characterization is done at the factory to make this technique simple. The exponential calibration technique utilizes a single calibration blend.